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Applicant: THE GOODYEAR TIRE & RUBBER COMPANY 1144 East Market Street Akron, Ohio 44316-0001(US)

Inventor: Sandstrom, Paul Harry 96 Milton Drive Tallmadge, Ohio 44278(US) Inventor: Francik, William Paul 491 Mackinaw Circle Bath, Ohio 44313(US)

Representative: Leitz, Paul
Goodyear Technical Center, Patent
Department
L-7750 Colmar-Berg(LU)

54) Pneumatic tire having air retention toeguard.

(57) A pneumatic rubber tire having an integral air retention toeguard outer layer of a sulfur cured rubber composition comprised of a blend of butyl and/or halobutyl rubber and epoxidized natural rubber.

### Field

This invention relates to a pneumatic tire having an air retention toeguard.

#### 5 Background

The toeguard of a pneumatic rubber tire is primarily an outer portion of the tire adjacent to its bead portion that contacts the rim of the wheel in a tire/wheel assembly. The toeguard is well known to those having skill in the tire art.

The inner surface of pneumatic rubber tires is typically comprised of an elastomeric composition designed to prevent or retard the permeation of air and moisture into the carcass from the tire's inner air chamber. It is often referred to as an innerliner. Innerliners have also been used for many years in tubeless pneumatic vehicle tires to retard or prevent the escape of air used to inflate the tire, thereby maintaining tire pressure.

An innerliner typically extends across the crown area of the inner portion of the tire as well as its sidewalls but does not typically extend entirely to the bead area. The toeguard portion, or component, of the tire generally extends into this area and the innerliner does not usually extend across the toeguard. The toeguard component is typically located at the bead region of the tire as an outer layer of the tire which interfaces with a rigid rim on which the pneumatic tire is mounted. It thus, in a sense, might be considered as an extension of the tire innerliner.

Rubbers which are relatively impermeable to air are often used as a major portion of said innerliners and can include butyl rubber and halobutyl rubbers. U.S. Patent Nos. 3,808.177 and 4,725,649 are instructive.

The innerliner is normally prepared by conventional calendering or milling techniques to form a strip of uncured compounded rubber of an appropriate width, which is sometimes referred to as a gum strip. Typically, the gum strip is the first element of the tire to be applied to a tire building drum, over and around which the remainder of the tire is built. When the tire is cured, such innerliner becomes an integral, cocured, part of the tire. Tire innerliners and methods of preparation are well known to those having skill in such art.

However, as hereinbefore pointed out, the protective innerliner designed to be an air barrier often does not extend to the bead area and particularly the toeguard area of the tire. This is sometimes because, during the building of the tire, the soft innerliner rubber compound can flow into a portion of the tire building machine near the bead portion of the tire being built making it difficult to remove the tire therefrom. An absence of such innerliner in the toeguard area can be a disadvantage because as the toeguard extends into or around the bead area, it typically then has substantially less air retention properties. A toeguard could, however, provide a valuable extension to the tire innerliner layer.

## Disclosure and Practice of Invention

In accordance with this invention, a pneumatic rubber tire is provided with an integral toeguard component layer of a sulfur cured rubber composition positioned as an outer layer of the tire in its bead region comprised of, based on 100 parts by weight rubber, a blend of (A) about 20 to about 60 parts by weight of at least one of butyl rubber and halobutyl rubber; and (B) about 80 to about 40 parts by weight of rubber comprised of (1) about 10 to about 100, preferably about 50 to about 100, weight percent epoxidized cis 1,4-polyisoprene rubber and, correspondingly, up to about 90, preferably up to about 50, weight percent cis 1,4-polyisoprene rubber, where said epoxidized rubber has a glass transition temperature (Tg) in the range of about -10° C to -60° C.

While the epoxidized cis 1,4-polyisoprene rubber or the cis 1,4-polyisoprene rubber (not epoxidized) may be either natural or synthetic rubber, preferably at least one is natural rubber.

The toeguard rubber composition of this invention was observed to have an enhanced resistance to air permeation. It thus provides a valuable extension of the tire innerliner to the bead region of the tire.

The Tg of the epoxidized cis 1,4-polyisoprene rubber, preferably natural rubber, is proportional to the level of epoxidation. Typically, the level of epoxidation is in the range of about 5 to about 50 mole percent usually at least about 20 mole percent, preferably about 20 to about 30 mole percent. The epoxidation of the natural rubber may be accomplished, for example, by epoxidation of natural rubber latex using peroxides which generate oxygen for the reaction. The level of epoxidation is the percent of the double bonds of the rubber which have been epoxidized.

Preferably, the halobutyl rubber is at least one of chlorobutyl and bromobutyl rubber. Such rubbers are

well known.

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In practice, the toeguard composition is generally first prepared as an uncured compounded rubber gum strip, usually fabric reinforced, constructed as an outer layer (exposed outside surface of the tire and positioned to contact the rim of the wheel, although once mounted on a rim, a part or even most of the toeguard may not be visible) of an uncured rubber tire structure in the region of its bead portion, and then sulfur co-cured with the tire during the tire curing operation under conditions of heat and pressure. Thus, the toeguard layer becomes an integral part of the tire by being co-cured therewith as compared to being a simple adherent laminate. Thus, the toeguard component is sulfur co-cured with the rubber tire carcass. Such toeguard location and construction is well known to those having skill in such tire art.

It is to be understood that the prescribed toeguard rubbers can be compounded with conventional rubber compounding ingredients comprised of, for example, carbon black, clay, talc, mica, silica, zinc oxide, stearic acid, rubber processing oil, sulfur, accelerator and antidegradant and then typically extruded and/or calendered to form the uncured gum strip. Such rubber compounding materials and methods are well known to those having skill in such art.

The toeguard component is typically fabric reinforced with a textile woven fabric. Various fabrics can be used, such as, for example, those of polyester, rayon, nylon or aramid.

The uncured tire carcass rubber interface with which the toeguard, particularly the fabric reinforced toeguard component, is sulfur co-cured can be of various sulfur curable rubber and rubber blends such as, for example, synthetic diene rubbers such as polybutadiene, polyisoprene and styrene/butadiene copolymer rubbers.

Thus, the toeguard component becomes an integral outer layer of the tire in that sense that it is a layer on the outer portion of the tire carcass, although when the tire is mounted on a rim most, if not all, of the toeguard component will not be readily visible.

The toeguard component rubber composition (fabric reinforced) can be an extension of or become a part of the tire's basic innerliner. It is important to appreciate that the fabric reinforced toeguard component of this invention is positioned to be located between the tire bead component and a rigid rim in a tire/rim assembly.

Typically the uncured toeguard strip has an uncured thickness in the range of about 0.03 to about 0.08 inch (0.08-0.2 cm), depending somewhat on the tire size and its intended use.

The pneumatic tire with the integral toeguard composition may be constructed in the form of a passenger tire, truck tire, or other type of bias or radial pneumatic tire.

The following examples are presented to demonstrate the invention. The parts and percentages are by weight unless otherwise noted.

### 55 EXAMPLE I

Samples of blends of halobutyl rubber with other rubbers (Experiments A-C), namely, natural rubber, and/or epoxidized natural rubber were prepared and tested as shown in Tables 1 and 2.

Experiments B-C show the results of blends of epoxidized natural rubber combinations with halobutyl rubbers such as 50/50 and 65/35 epoxidized natural rubber/halobutyl ratios. The halobutyl rubber used was bromobutyl rubber.

They illustrate improvements over a control (Exp A) and the blend of Experiment B showed an advantage over all the others for air impermeability.

The materials were mixed as a two-step mixing process in a rubber blender in which all of the ingredients were mixed in the first step except for sulfur, accelerators and zinc oxide which were added and mixed in the second step.

The physical tests were conducted on the cured samples (the samples were prepared by curing the rubber for about 18 minutes at  $150\degree$  C) using conventional methods.

The following Table 1 demonstrates the recipes of which the samples were comprised. Experiments B-O C represent variations of the compositions used to demonstrate the invention.

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Table 1

_	Matania 1	<u>Control</u>	Parts	
5	<u>Material</u>	Exp A	Exp B	Exp C
	Natural Rubber	50	0	0
10	Epoxidized Natural Rubber	0	50	65
	Halobutyl Rubber <sup>2</sup>	50	50	35
	Carbon Black	45	45	45
15	Silica	25	25	25
20	Processing Oil (Napthenic)	10	10	10
	Antidegradant (p-phenylene diamine type)	2	2	2
25	Zinc Oxide	4	4	4
	Stearic Acid	2	2	2
30	Sulfur	2	2	2
	Accelerator (sulfenamide type)	1	1	1

- 1. Obtained as 25% epoxidized natural rubber, (25% of double bonds epoxidized), obtained from MRPRA, or Malaysian Rubber Producers Research Association.
- 2. Obtained as high viscosity, brominated isobutylene isoprene rubber from Polysar Ltd.

Various tests were conducted on the prepared, cured samples. The results are shown in Table 2, with Exp D (an additional Control) and Exp A-C relating to the samples of Exp A-C of Example I, with Exp A being a control in Example I for comparative purposes and Control Exp D is a formulated cured blend of natural rubber and styrene/butadiene copolymer rubber as a representative pneumatic tire toeguard compound which was not especially formulated for air retention emphasis for this example.

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Table 2

5	<u>Properties</u>	Control) Exp D	Exp A	Exp B	Exp C
	Air Permeability (cc.mm/in day.atm)	970	340	150	180
10	Tear <sup>1</sup>	13	30	15	15
	Adhesion to $Liner^2$	69	60	61	60
15	200% Modulus (MPa)	11	9.7	10.5	10
	Tensile (MPa)	13.4	14	12.4	12
20	Elongation @ Break (percent)	240	450	230	270
	Rebound	26	23	19	20

- 1. The tear value was determined by a peel tear test which measures the force in newtons to separate two similar cured sheets, pulling one sheet away from the other at a 180 degree angle. Such type of test is well known to those having skill in rubber compound test procedures.
- 2. The adhesion value was determined by peel tear test of the sample to a tire liner compound, represented in Newton units and is otherwise conducted in a manner similar to the aforesaid peel tear test for the aforesaid tear value test.

Air permeability tests were conducted by measuring the amount of air which permeates a thin rubber sample in a prescribed time under prescribed conditions as indicated above. Such type of test is understood to be well known to those having skill in such art.

Thus, these results demonstrate that use of epoxidized natural rubber improves the air impermeability over that of natural rubber and a more typical type of toeguard compound formulation.

A pneumatic rubber tire was prepared with its toeguard having an outer layer having the composition similar to Exp B and with textile woven fabric reinforcement.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

### Claims

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1. A pneumatic rubber tire with an integral toeguard component as a layer of a sulfur cured rubber

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composition positioned as an outer layer of the tire in its bead region characterized by being comprised of, based on 100 parts by weight rubber, a blend of (A) about 20 to about 60 parts by weight of at least one of butyl rubber and halobutyl rubber; and (B) about 80 to about 40 parts by weight of rubber comprised of (1) about 10 to about 100 weight percent epoxidized cis 1,4-polyisoprene rubber and, correspondingly, up to about 90 weight percent cis 1,4-polyisoprene rubber, where said epoxidized rubber has a glass transition temperature (Tg) in the range of about -10° C to about -60° C.

- 2. The tire of claim 1 characterized in that said epoxidized natural rubber has a level of epoxidation in a range of about 5 to about 50 mole percent.
- 3. The tire of claim 2 characterized in that said toeguard component is fabric reinforced.
- 4. The tire of claim 3 characterized in that at least one of said epoxidized cis 1,4-polyisoprene rubber and said cis 1,4-polyisoprene rubber is natural rubber and said halobutyl rubber is selected from at least one of chlorobutyl and bromobutyl rubber.
- 5. The tire of claim 3 characterized in that said toeguard component is positioned to be located between the tire bead component and a rigid rim in a tire/rim assembly.
- 20 6. The tire of claim 3 characterized in that said toeguard component is sulfur co-cured with the rubber tire carcass.
  - 7. The tire of claim 4 characterized in that said toeguard component is sulfur co-cured with the rubber tire carcass.
  - 8. A pneumatic rubber tire is provided with an integral toeguard component as a layer of a sulfur cured rubber composition positioned as a textile woven fabric reinforced outer layer of the tire in its bead region characterized by being comprised of, based on 100 parts by weight rubber, a blend of (A) about 20 to about 60 parts by weight of at least one of butyl rubber and halobutyl rubber where said halobutyl rubber is selected from at least one of chlorobutyl rubber and bromobutyl rubber; and (B) about 80 to about 40 parts by weight of rubber comprised of (1) about 50 to about 100 weight percent epoxidized cis 1,4- polyisoprene rubber and, correspondingly, up to about 50 weight percent cis 1,4-polyisoprene rubber, where said epoxidized rubber has a glass transition temperature (Tg) in the range of about -10 ° 6 to about -60 ° C and where said epoxidized rubber has a level of epoxidation in the range of about 20 to about 50 mole percent.
  - 9. The tire of claim 8 characterized in that at least one of said epoxidized cis 1,4-polyisoprene and cis 1,4-polyisoprene is natural rubber.
- 40 10. The tire of claim 8 characterized in that said toeguard component is positioned to be located between the tire bead component and a rigid rim in a tire/rim assembly.
  - 11. The tire of claim 8 characterized in that said toeguard component is sulfur cured with the rubber tire carcass.

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# EUROPEAN SEARCH REPORT

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gory		i indication, where appropriate, ant passages		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CI.5)	
Υ	FR-A-2 624 440 (UNIROYA * Page 1, line 33 - page 5, lir			1-11	B 60 C 1/00 B 60 C 5/14	
Υ	CH-A-3 278 26 (J.J. HOES * Claims I-II; figure; page 2, I			1-11	B 60 C 5/16	
Α	US-A-4 396 051 (M. OGAV * Claims 1-4; table 3 *	/A et al.)		1,4,6-8, 11		
Α	GB-A-2 113 692 (MALAYS RESEARCH ASSOC.) * Claims 1-10; page 3, line 3		RS	1-2,4,8-9		
Α	EP-A-0 251 980 (GOODYE * Column 5, lines 27-65; figu			1,3,8		
					TECHNICAL FIELDS SEARCHED (Int. Cl.5)	
					B 60 C C 08 G C 08 J	
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	The present search report has t	een drawn up for all claims				
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O: P:				<ul> <li>member of the same patent family, corresponding document</li> </ul>		